

Determination of Rhenium in Environmental Samples Using an Extraction Chromatographic Resin and ICP-MS

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A simple separation method for Re determination in rock and seawater samples by inductively coupled plasma mass spectrometry (ICP-MS) has been developed. An extraction chromatographic resin (TEVA resin, Eichrom Ind. Inc.) was employed to separate Re from sample matrices and trace elements that cause isobaric interference during ICP-MS measurements. Total average yields were $94 \pm 3\%$ for rock and soil samples and almost 100% for water samples. The method was applied to trace-level Re determination in standard igneous rock and seawater samples. The measured Re values were 0.05 - 4.0 ng/g for the rock samples and 6.3 - 12.7 pg/mL for the seawater samples.

INTRODUCTION

Rhenium is known as one of the rarest elements in earth's surface. The earliest measurements of Re were made using radiochemical neutron activation analysis (RNAA). However, the scarcity and the analytical difficulty limited the data available from environmental samples by this method. More recently, inductively coupled plasma mass spectrometry (ICP-MS), resonance ionization mass spectrometry (RIMS) and negative thermal ionization mass spectrometry (N-TIMS) have been applied. Especially in the last decade, the amount of Re data in environmental rock samples has notably increased mainly due to the instrumental development. ICP-MS is easier to operate than other instruments, such as RIMS and N-TIMS, that have similar detection limits for Re.

Even though ICP-MS can measure trace levels of Re, the element must be separated from sample components that interfere with Re measurement. There are several Re separation methods, including acid digestion or fusion of the sample followed by solvent extraction and anion-exchange.¹⁻⁶ The anion-exchange step is necessary because some solvent extraction procedures result in organic contamination in the final solution used for ICP-MS or N-TIMS. The resin separation gives satisfactory purity but requires more sample, which can increase background level. Moreover, combinations of solvent extraction and ion-exchange complicate Re separation schemes.

This paper presents results from a novel and simpler method that gives consistently high Re recovery from rock/soil and seawater samples analyzed with ICP-MS. The procedure includes an extraction chromatographic resin (TEVA resin, Eichrom Ind. Inc.) previously identified as having a high selectivity for Re and Tc.⁷

EXPERIMENTAL

Reagents

Nitric acid was super-pure grade (AA-100, Tama Chemicals). Sodium carbonate and NH_4OH were of analytical reagent grade. The Re concentrations in super-pure HNO_3 and NH_4OH used in this study were below the limit of detection by ICP-MS. Water ($>17 \text{ M}\Omega$) treated using a Milli-Q water system (Millipore Co.) was used throughout. This water was also used to rinse all beakers and vials. A packed TEVA resin column that was charged with 2 mL TEVA resin and pretreated with 5 mL of 8M HNO_3 and 5 mL of 0.1M HNO_3 .

A Re tracer solution was obtained by dissolving NH_4ReO_4 powder (Wako Chemicals Co.), ca. 1 g, in a known amount of Milli-Q water with addition of a small portion of hydrogen peroxide solution. To make a standard curve for ICP-MS measurement, a series of five standards for Re of known concentrations (1 – 100 ppt) were prepared by diluting a multi-element standard solution, XSTC-8 (SPEX Ind. Inc.), with 2% HNO_3 .

Samples

Because there is no standard environmental reference material with a known Re content, results of our methods were compared to others in the literature for which samples were available. Seawater sampling was carried out on the coasts of Hitachinaka, Chiba and Izumisano in Japan. The seawater samples were collected in acid-cleaned 0.5- or 1-L polypropylene bottles. Rock samples used were standard igneous rocks found in Japan and prepared by the Geological Survey of Japan. Their code numbers were, JB-1, JB-3, JG-1 and JR-2. Two Japanese agricultural soil samples, Soil-1 and Soil-2, classified as humic cambisol and orthic Acrisol, respectively, were used in recovery tests. Before testing, the soils were air-dried, sieved with a 2 mm mesh and then ball milled into fine powder.

Elution behavior of Re from TEVA resin

The Re elution behavior was evaluated using the TEVA resin column. A 250-mL aliquot of ReO_4^- solution (10 ppb Re in 0.1 M HNO_3) was loaded to the column at a flow rate of ca. 1.4 mL/min. Then, the column was washed with 40 mL of 1, 2, 4 or 8 M HNO_3 . Finally, Re retained in the column was stripped with 10 mL of 12 M HNO_3 . The Re concentrations in all eluates were measured by ICP-MS (PMS-2000, Yokogawa).

Analytical techniques

Seawater samples. Immediately after collecting the samples, they were transferred to our laboratory, then they were pressure filtered through 0.2 μm Millipore[®] filters. About 500-mL was transferred to a 1-L beaker and weighed accurately. The sample was acidified with 0.5 mL conc. HNO_3 and 50 μL of H_2O_2 per 100 mL. The solution was boiled on a hot plate for 1 h to convert Re chemical forms into ReO_4^- . After the sample had cooled to room temperature, it was passed through the TEVA resin column and the column was washed with 40 mL of 0.8M HNO_3 . The Re fraction was then eluted with 5 mL 8M HNO_3 . Finally, the solution was diluted 10 or 20 times with deionized water prior to analysis by ICP-MS.

Rock samples. A known weight of rock sample (ca. 0.5 - 1 g) was placed in a platinum crucible and a certain amount of Na_2CO_3 (about 5 - 6 times the sample volume) was added with thorough mixing. The mixture was fused for 1 h in a molten state over a Bunsen burner flame. After cooling, the cake was transferred with water from the crucible to a glass beaker. The mixture was acidified with 8M HNO_3 solution until the pH reached 1-2. The sample was filtered through a glass fiber filter (GF-A, Whatman plc.) and the residue was discarded. Then, the filtrate was neutralized with NH_4OH and the iron hydroxide precipitate was removed using another glass fiber filter. The Re in the filtrate was separated using the TEVA resin column as described above. The nitric acid solution (ca. 5 mL of 8M HNO_3), used to strip the TEVA resin, was evaporated to near dryness on a hot plate at 90°C. The residue was dissolved in 5 mL of 0.1M HNO_3 before introducing it into the ICP-MS. Total procedural blanks for Re ranged from 2.1 – 7.9 pg/g sample for this method.

Apparatus

The Re concentration in the solutions was determined with the ICP-MS. For the quantitative determination of Re, $m/z = 185$ and 187 were scanned for 20 s and 60 s, respectively, with a number of sweeps of 1000 for one scan. The scan was repeated 4 times. The Re contents were determined using counts obtained at mass 187. The instrumental detection limit was 0.2 pg/mL.

RESULTS AND DISCUSSION

Elution behavior of Re from TEVA resin

The elution behavior of Re is summarized in Fig. 1. When the sample solution, ca. 0.1 M HNO_3 , was introduced to the resin column, Re adsorbed onto the resin completely. Thus, no Re was found in the eluate. Then the column was washed 5 times with 8 mL of 1, 2, 4 or 8 M HNO_3 . When 1 M HNO_3 was used, Re was well retained by the resin. However, Re sorbed on the resin was gradually removed by 2 M HNO_3 . At higher concentrations of HNO_3 , Re was easily removed from the resin with less than 8 mL of eluant. It has been previously reported that Tc was strongly sorbed onto the resin column even when 40 mL of 2 M HNO_3 was introduced to wash the column.⁹ The results of the column experiment support the finding of different k' values for Tc and Re as we reported before.⁷ Thus, when the TEVA resin is applied for Re separation, <1M HNO_3 should be used to wash the column.

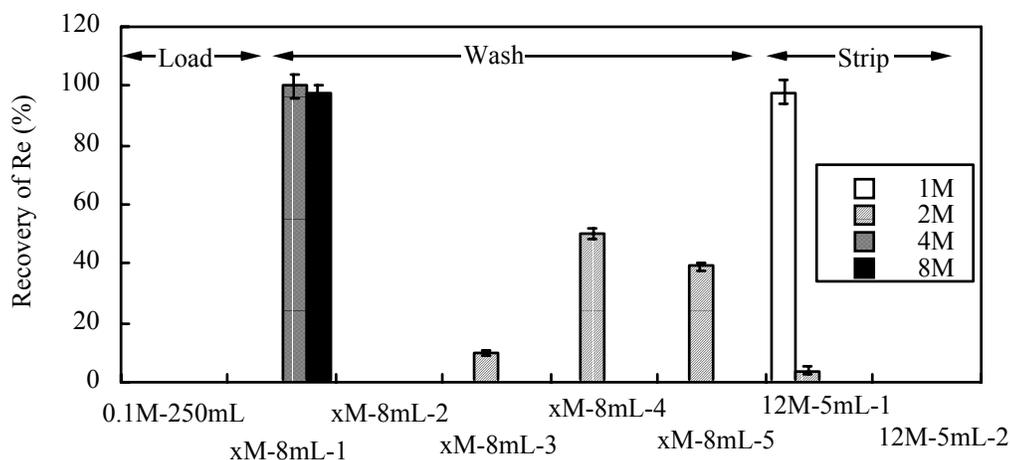


Fig. 1 Recoveries of Re in wash and strip solutions when nitric acid concentrations for wash were 1, 2, 4 and 8M.

Note: Error bars show counting error (1 sigma).

Total chemical recoveries of Re in environmental samples

Seawater samples. As described above, almost 100% recovery was observed for deionized water samples with ReO_4^- . We also carried out a radiotracer experiment using seawater samples and the average recovery was almost 100%, while interferences for ICP-MS measurement, such as rare earth elements and W, were eliminated. Thus, Re was purified from water samples without any loss by the resin separation method.

Rock samples. Overall chemical recoveries of Re from rock samples were compared using elevated concentrations of Re (0.9 μg or 1.8 mg for a sample). These results are shown in Table 1. Although the concentrations differed by three orders of magnitudes from each other, the recovery of Re was almost the same. Thus, in the separation scheme, there was no mass effect on Re purification. The average recovery by the method developed here was $94 \pm 3\%$. It was clear that Re recovery remained constant through the separation steps after fusion, although matrix compositions were different. This might be explained by the chemical form of Re; the element was probably in ReO_4^- when the fused mixture was dissolved into an aqueous solution. However, about 3% of the initial amount of Re was passed through with the sample solution. In alkaline solution, ReO_4^- is the dominant chemical species so that Re should be extracted onto the resin completely. The result suggests that a small amount of Re might be in other chemical forms. Some matrix elements and/or anions in the rock and soil sample solutions can affect the Re speciation. Further studies are needed to clarify why this loss was observed.

Table 1. Overall recoveries of Re from rock and soil samples obtained by using two different Re concentrations

Sample	Re-0.9 μg /sampl	Re-1.8mg/sampl
	e (%)	e (%)
JB-1	97.8 \pm 0.7	96.0 \pm 1.5
JG-1	not measured	90.5 \pm 1.8
Soil-1-1st	94.1 \pm 1.6	94.4 \pm 1.9
-2nd	94.1 \pm 2.1	
-3rd	91.4 \pm 3.3	
Soil-2	94.1 \pm 2.8	95.4 \pm 1.5
Average	94.3 \pm 2.3	94.1 \pm 2.5

\pm values show counting error (1sigma).

Determination of Re in seawater samples

The Re concentrations in seawater samples were shown in Table 2. Previous results reported in the literature are also listed. The measured values by our method were 6.3-12.7 ng/kg, within the range of previous data. The result is reasonable, as it has been reported by several authors that Re behaves conservatively in seawater because of its chemical form.^{3, 12, 14} However, it is not clear why the values varied by a factor of 2. This might be affected by Re supply from the air, fixation or transformation of Re by organic matter and sulfide, etc. Research is in progress that should clarify this.

Table 2. Rhenium concentration in seawater.

Location	Re (ng/kg or ng/L)		Reference
	Min.-Max.	Average	
Pacific Ocean	7.2 – 10.2	8.4	Scadden, 1969 ¹⁰
Atlantic Ocean	5.9 – 8	6.9	Matthews and Riley, 1970 ¹¹
Pacific Ocean	5.3 – 15.2	9.1	Koide <i>et al.</i> , 1987 ¹²
Pacific Ocean	7.5 – 8.5	8.0	Shabani and Masuda, 1992 ¹³
Pacific Ocean	7.33 – 7.70	7.42	Anbar <i>et al.</i> , 1992 * ¹⁴
Atlantic + Pacific	-	8.24 +/- 0.07	Colodner <i>et al.</i> , 1993 * ³
Pacific Ocean	6.3 – 12.7	9.5	This study

* Values are reported on a salinity-normalized basis.

Determination of Re in rock and soil samples

The developed separation method was used to measure the Re content in five standard igneous Japanese rock samples, without addition of Re tracer; the average recovery of $94 \pm 3\%$ was applied to these samples. Sample amounts used were 0.5 - 1 g. Each sample was analyzed at least twice. The observed values in this study are shown in Fig. 2 and the Re values ranged from 0.05 to 4.0 ng/g. The replicates are in good agreement, indicating that the method is reproducible. The values obtained in this study were compared with literature values determined by RNAA.⁸ Ratios between the observed values in this study to those in literature were 0.75 - 3. No systematic error was found between the determination methods, ICP-MS and RNAA. This suggests that the accuracy of our method is reasonable. However, one reason for small discrepancies could be ascribed to matrix components in rock and soil samples. According to private communication with the authors,⁸ their reported values were based on few data and are therefore provisional. More data are required for discussion on the slight differences between the two methods.

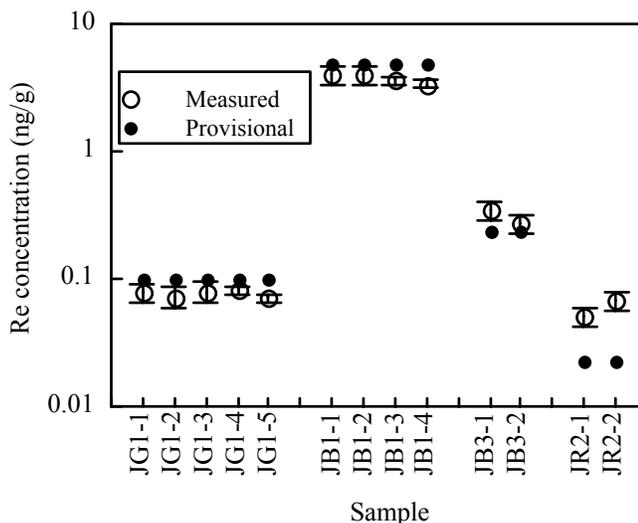


Fig. 2 Rhenium concentrations in standard Japanese igneous rock samples.

Note: Error bars show total error (1 sigma).

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